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Measurement of Volatile Organic Compounds
Supplement 1

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

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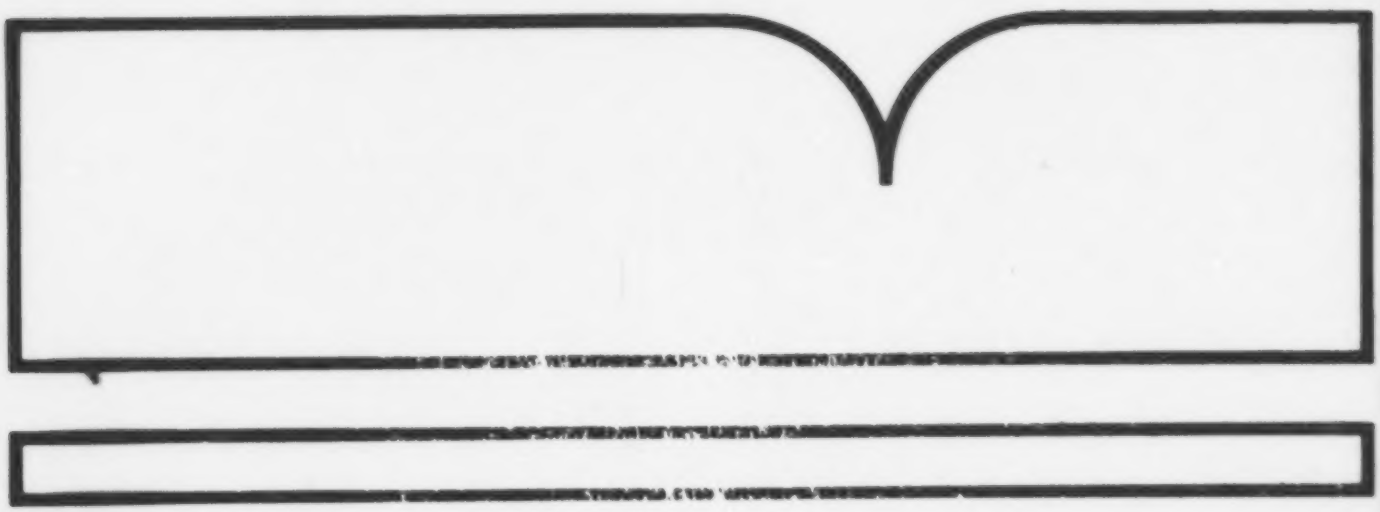

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Guideline Series

Measurement of Volatile Organic Compounds - Supplement 1

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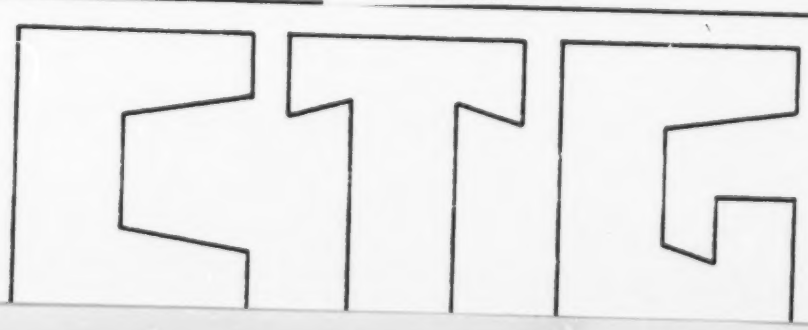

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16. ABSTRACT

This document consists of three test methods that the Environmental Protection Agency believes have a wider range of application as written than the reference methods promulgated by the Agency in the course of developing national performance standards for specific source categories. While these three methods do not contain source specific application instructions, they can, with proper consideration as alternate or screening methods, produce results that in many instances are adequate for determining compliance. The methods are "General Measurement of Total Gaseous Organic Compound Emissions Using a Flame Ionization Analyzer," "Determination of Selected Volatile Organic Emissions by the Adsorption Collection Technique," and "Approximate Determination of Selected Volatile Organic Emissions Using Detector Tubes."

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Measurement of Volatile Organic Compounds - Supplement 1

Emission Measurement Branch
Emission Standards and Engineering Divison

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

July 1982

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PREFACE

Emphasis on the control of volatile organic compounds through the State Implementation Plans, new source performance standards, and national emission standards for hazardous air pollutants has created a need for standardized test procedures. In setting national performance standards for new sources, and national emission standards for hazardous air pollutants, the Environmental Protection Agency has followed a policy of establishing a reference method for each regulated source category and pollutant. These source specific test methods generated by the Environmental Protection Agency do not always provide the type of general application test methods that are more likely to satisfy the measurement method guidance needed by the States in their efforts to implement their own regulations for sources emitting volatile organics.

The purpose of this supplemental document, therefore, is to continue to provide guidance to the States on the measurement of volatile organic compounds from a diversity of sources and pollutants that is consistent with the methodology being applied by the Environmental Protection Agency as it develops regulations for specific sources and pollutants.

This document is a supplement to Measurement of Volatile Organic Compounds, EPA-450/2-78-041, September 1979.

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INTRODUCTION

This document consists of three test methods for the measurement of volatile organics that the Environmental Protection Agency believes have a wider range of application than the reference methods promulgated by the Agency in the course of developing national performance standards for specific source categories. While these three methods do not contain source specific application instructions, they can, with proper consideration as alternate or screening methods, produce results that in many instances are adequate for determining regulatory compliance.

The first method, "General Measurement of Total Gaseous Organic Compound Emissions Using a Flame Ionization Analyzer," can be applied to a wide variety of sources in ways that will yield results that are appropriate to many volatile organic regulations.

The second method, "Determination of Selected Volatile Organic Emissions by the Adsorption Collection Technique," builds on ambient air sampling and analysis techniques from the National Institute of Occupational Safety and Health series of test methods to devise a similar test method for stationary source conditions.

The third method, "Approximate Determination of Selected Volatile Organic Emissions Using Detector Tubes," is a general procedure for the application of detector tubes to stationary sources that recognizes the possible deficiencies of detector tubes in this application. This method fits the "screening method" category, which means that while the method may produce biased or inprecise results, control agencies may, on occasion, find it adequate for compliance determinations.

GENERAL MEASUREMENT OF TOTAL GASEOUS ORGANIC

COMPOUND EMISSIONS USING A FLAME IONIZATION ANALYZER

1. Applicability and Principle

1.1 Applicability. This method can be used to determine total gaseous organic compound volume or mass stack gas emission concentration in terms of carbon, methane, propane, or a source-specific organic compound.

If the instrument is calibrated with mass concentration standards prepared with a source-specific organic and then used to measure emissions of that organic, the results represent actual mass concentrations of that organic. Since the detector responds to nearly all organics, a supplemental measurement is necessary if it is desired to exclude any particular organic(s) from the final result.

Application to sources emitting varying amounts of two or more organic compounds that have considerably different response factors will produce ambiguous results. Particular care should be exercised in the choice of equipment and operation in potentially explosive atmospheres.

1.2 Principle. The sample is extracted from the source through a heated (if necessary) sample line and glass fiber filter into a flame ionization analyzer (FIA). In the FIA, the combustion of a specific organic compound in a H_2/O_2 flame forms ions that establish a current proportional to the mass flow rate of that organic to the flame. The ions are collected on two polarized electrodes, and the current is

measured on a potentiometric recorder and compared with a calibration curve based on propane (C_3H_8), or a source-specific organic, as appropriate. The results are reported as volume or mass concentration equivalents of methane (CH_4), propane, carbon, or the source-specific organic.

2. Range and Sensitivity

2.1 Range. Signal amplification and attenuators shall be available so that a minimum signal response of 10 percent of full scale can be produced when analyzing calibration gases or samples.

2.2 Sensitivity. The detector sensitivity shall be equal to or better than 2.0 percent of the full-scale setting, with a minimum full-scale setting of 10 ppm (methane or carbon equivalent).

3. Interferences

3.1 Inorganic Gases. The FIA does not respond to nitrogen, carbon monoxide, carbon dioxide, or water vapor, but its response to organics is affected by the composition of the background or carrier gas. Therefore, the calibration gases shall be contained in air if air is the major component of the emission sample.

A mixed fuel (either 40 percent H_2/60 percent N_2 or 40 percent H_2/60 percent He) may be helpful in reducing response variability due to changes in the sample or carrier gas composition.

3.2 Organic Compounds. Acetylenic compounds give a slightly higher response than aliphatic compounds. Carbon atoms bound to oxygen, nitrogen, or halogens give a reduced or zero response. Aldehydes produce little, if any, response on a FIA.

Table 1 illustrates these effects in terms of the relative response of one FIA to various hydrocarbons. The response is shown as effective carbon number (ECN), as follows:

$$ECN = \frac{\text{Instrument response caused by atom of given type}}{\text{Instrument response caused by aliphatic carbon atom}}$$

These values shall be available for the specific detector used under "as used" conditions (e.g., mixed H_2/H_e fuel). These numbers can vary widely for different operating conditions and for different detectors. For example, variations of as much as 25 percent have been observed in studies of the types of organics associated with automotive emissions (see Citation 9.6 under Bibliography).

Table 1 also illustrates that the accuracy of this method for a given source is largely dependent on knowledge about the particular makeup of organic emissions from the source.

When two or more compounds are present in the emissions, it is advisable to consider whether or not the standards generated by the procedure described in Section 7.3 provide the compounds in the same relative proportions (mole fraction) as they exist in the emissions. If not, or if the relative proportions of each compound are changing with time in the emissions, then consideration should be given to the substitution of a gas chromatographic analytical procedure. Each organic in an air emission contributes to a total FIA response as follows:

Table 1. APPROXIMATE EFFECTIVE CARBON NUMBERS

(FROM BECKMAN INSTRUMENTS)

Type of atom	Occurrence	Effective carbon number
Carbon	In aliphatic compound	+1.0
Carbon	In aromatic compound	+1.0
Carbon	In olefinic compound	+0.95
Carbon	In acetylenic compound	+1.30
Carbon	In carbonyl radical	0.0
Carbon	In nitrile	+0.3
Oxygen	In ether	-1.0
Oxygen	In primary alcohol	-0.6
Oxygen	In secondary alcohol	-0.75
Oxygen	In tertiary alcohol, ester	-0.25
Chlorine	As two or more chlorine atoms on single aliphatic carbon atom	-0.12 each
Chlorine	On olefinic carbon atom	+0.05
Nitrogen	In amine	Value similar to that for oxygen atom in corresponding alcohol

$$R_{cx} = \text{mole } f_{cx} \left[\frac{\Sigma \text{ ECN}_{cx}}{M_{cx}} \right]$$

Where:

R_{cx} = Response due to the presence of a particular compound.

mole f_{cx} = Fraction of the emissions or calibration standards contributed by a particular compound (mole basis).

Σ ECN_{cx} = Summation of the effective carbon numbers of the atoms which constitute a molecule of a particular compound.

M_{cx} = Molecular weight of a particular compound.

By comparing Σ R_{cx} for the standards to Σ R_{cx} for the emissions, one can determine the extent to which ambiguities can be expected in concentration and mass rate measurements. This comparison should be made regardless of the number of compounds in the calibration gas. This information can be obtained through study of comparative analyses with gas chromatography on a source category basis.

3.3 Other Effects. Significant changes in viscosity of the sample gas from that of the calibration gas could change gas volume flow rate and therefore the mass rate of organics to the detector. If this phenomenon is expected to occur, make provisions to change the calibration procedures to identify and correct it.

4. Apparatus

4.1 Flame Ionization Analyzer. Adaptable to field use, with heat traced sample piping. The analyzer shall be demonstrated, preferably by the manufacturer, to meet or exceed manufacturer's specifications and those described in Section 6.1 of this method.

The entire sampling and analytical system exposed to gaseous organics shall be capable of being maintained in a temperature range consistent with the particular measurement requirements to prevent condensation and minimize adsorption in sampling lines.

4.2 Sample Conditioning or Interface System. Probe, with filter, stainless steel or Teflon sample line, three-way valve for introducing calibration gas, Teflon-coated diaphragm pump or stainless steel bellows pump, and stainless steel flow control valves, capable of being maintained in a temperature range consistent with the particular measurement requirements.

4.3 Barometer and Bubble Tube Flowmeter. To establish volume flow rate to detector.

4.4 Recorder (optional). Strip chart recorder with a voltage input compatible with the FIA. Other recording devices may be used provided that the minimum data-recording rate is one measurement value per minute.

4.5 Calibration. Sections 4.5.2 through 4.5.6 are for the optional procedure in Section 7.3.

4.5.1 Tubing. Teflon, 6.4-mm outside diameter, separate pieces marked for each calibration concentration.

4.5.2 Tedlar or Aluminized Mylar Bags. Fifty-liter capacity, with valve, separate bag marked for each calibration concentration.

4.5.3 Syringe. 5 µl, individually calibrated to dispense liquid organic.

4.5.4 Syringe. 25 µl, individually calibrated to dispense liquid organic.

4.5.5 Dry Gas Meter, with Temperature and Pressure Gauges. Accurate to ±2 percent, to meter nitrogen in preparation of standard gas mixtures, calibrated at the flow rate used to prepare standards.

4.5.6 Midget Impinger/Hot Plate Assembly. To vaporize liquid organic.

5. Reagents

5.1 Fuel. H_2 produced by a H_2 generator, or a 40 percent H_2/60 percent He or 40 percent H_2/60 percent N_2 mixture.

5.2 Combustion Air. High-purity air. Always required if the emission stream does not contain sufficient oxygen, and may be required by the analyzer. Supplemental support air may yield more stable operation of the analyzer.

5.3 Zero Gas. High-purity air with less than 0.1 ppm organics (methane or carbon equivalent).

5.4 Calibration Gases. Two gas mixture standards with volume concentrations corresponding to ranges of 5 to 10 ppm (methane or carbon equivalent) and 1.5 to 2.5 times the expected stack gas concentration, prepared and certified by direct cylinder analysis by a gas manufacturer. The latter concentration is hereafter referred to as the span gas. The standards will normally consist

of propane in air. Other organic(s) may be used, if appropriate. The gas manufacturer shall recommend a maximum shelf life for each cylinder so that the concentration does not change by more than ±2 percent from the certified value. The date of gas cylinder preparation, certified propane concentration, and recommended maximum shelf life shall be affixed to the cylinder before shipment from the gas manufacturer to the buyer.

5.5 Low Pressure Propane Cylinder and Dilution System. Alternative for generating calibration gases. Refer to Section 7.2.

5.6 Source-Specific Organic. Either a sample obtained from the source, or a sample distilled from paint, ink, etc., in accordance with ASTM Procedure D3272-73T. Vacuum distillation may be more appropriate. This item is only required when unaltered emissions of a specific organic are being measured, and mass calculations in terms of that organic are necessary.

6. System Performance Specifications

6.1 Linearity. Within ±5 percent of the expected value, up to the maximum percent absolute (methane or carbon equivalent) calibration point. Each analyzer shall be demonstrated before initial use to meet this specification using a four-point (minimum) calibration, with at least one calibration point in each of the following ranges: 5 to 10, 50 to 100, 500 to 1,000, and 5,000 to 10,000 ppm (methane or carbon equivalent). Certification of such demonstration by the manufacturer is acceptable. Additional calibration points that encompass emission values outside of these ranges shall be included, as necessary.

6.2 System Zero Drift. Not to exceed ±1 percent full scale or ±5 percent of stack gas reading, whichever is more, per test period.

6.3 System Span Drift. Not to exceed ±3 percent full scale or ±5 percent of stack gas reading, whichever is less, per test period.

7. Procedure

7.1 Sampling. Locate the FIA in a suitably protected environment. Assemble the system as shown in Figure 1. Install the sample probe in the stack with the probe opening(s) centrally located. Maintain a tight seal around the probe where it enters the stack. An in-stack filter shall be attached to the probe if any particulate matter is present. A sample may also be collected according to the procedure described in Method 23 (45 FR 39776, June 11, 1980) provided it can be demonstrated that bag wall losses do not exceed 5 percent from the time of collection to the time of analysis. For operating instructions specific to the FIA being used, refer to the manufacturer's manual.

Adjust the sample conditioning and analyzer heating systems to provide a temperature consistent with the measurement requirements, and allow the systems to warm up.

Before sampling, perform a leak check as follows: Recheck to confirm that all fittings are tight. With the sample probe plugged, close the flow control valve and open the excess sample bleed valve. Use leak detection fluid or immerse the tubing leading from the bleed valve in a jar of water to check that sample flow has ceased.

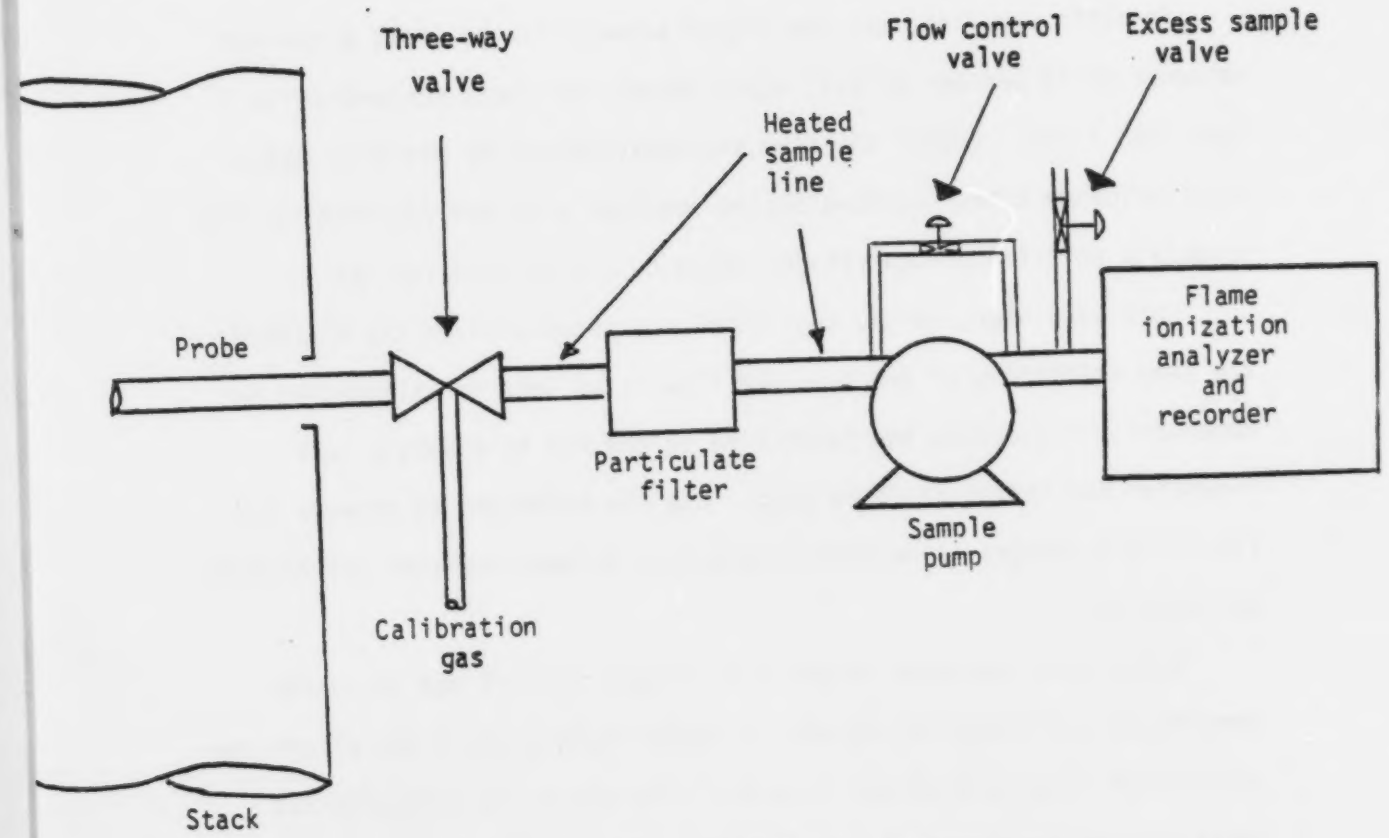

Figure 1. Flame Ionization Analyzer System.

Other leak check procedures can be used provided that they conclusively establish and demonstrate a no-flow situation. At the conclusion of sampling, recheck for leaks. If leaks have developed, void the run.

To begin sampling, set the signal attenuation to yield a minimum response of 10 percent of full scale unless the stack concentration is less than 1 ppm. Adjust the flow and bleed valves to minimize sample line residence time. Compare system readings with the calibration line to obtain emission concentrations based on the calibration gas.

Once each hour, verify that sample is introduced to the FIA under the same conditions of pressure and flow rates used in calibration by momentarily connecting the inlet line to the FIA to a bubble tube flowmeter and noting the flow rate. Use the barometer to observe any significant changes in barometric pressure between pre-test calibration and sampling.

System zero and span values will change or drift due to system temperature and pressure changes, or other factors which can affect the sample mass flow rate to the detector. Therefore, periodically (at least once an hour) introduce zero and span gases to the analyzer during each test period to determine zero and span drifts. If the analyzer has drifted beyond the allowable performance specification, consider the data collected since the last zero and span check to be invalid, unless the drift can be attributed to a quantitatively known change in temperature, pressure, or sample mass flow rate to the detector. Repeat the zero and span drift checks at the conclusion of the test period. Make no adjustment of the zero or span controls without noting the extent of the drift and the time of adjustment.

7.2 Pretest Calibration and Linearity Performance Check. Within 1 hour before the start of the first test period, construct a calibration curve as follows: With the signal attenuation at the most sensitive setting, introduce zero gas and adjust the respective zeroing controls to indicate a reading of less than 1 percent of full scale. With the signal attenuation at a sensitive setting, introduce the 5- to 10-ppm cylinder calibration gas and adjust the span control to yield a reasonable response value for that concentration on the analyzer readout. Repeat these two steps until adjustments are no longer necessary. Calculate a predicted response for the cylinder span gas, then introduce that gas and note the value obtained on the expected signal attenuation setting. If the value is not within ± 5 percent of its predicted value, then the analyzer may need repairs, or one or both of the calibration gases may need replacement. In any event, this linearity performance check specification shall be met before the analyzer is used for the test. Draw a straight line through the two calibration gas points and zero as derived by the least squares method.

As an alternative procedure, a low pressure high concentration propane cylinder standard and a dilution system calibrated with bubble tube flowmeters may be used to construct a three-point calibration curve. Start with the cylinder standard and then predict the response values for the two calculated dilutions. Apply the ± 5 percent criteria described above. Draw a straight line through the three calibration gas points and zero as derived by the least squares method.

7.3 Source-Specific Organic Standard Gas Mixtures. (Optional--see Sections 1.1 and 5.6). This procedure is applicable only where the

extent of bag wall surface adsorption/condensation of the organic compound is known.

7.3.1 Preparation of Standards. Assemble the apparatus shown in Figure 2. Evacuate a 50-liter Tedlar bag that has passed a leak check (described in Section 7.3.2), and meter in about 50 liters of air. Measure the barometric pressure, the relative pressure at the dry gas meter, and the temperature at the dry gas meter. While the bag is filling, use the 25-µl syringe to inject 10 µl of the liquid organic through the septum on top of the impinger. First slightly overfill the syringe, then invert it and depress the plunger to the 10 µl mark to dispel any air bubbles, and then inject. This gives a concentration somewhat less than 200 µg/liter. In a like manner, use the 5-µl syringe to prepare dilutions having approximately 40- and 20-µg/liter concentrations. To calculate the specific concentrations, refer to Section 8.2.

Alternatively, use an analytical balance to weigh the syringe before and after injecting the organic into the bag.

These gas mixture standards may be used for a few days from the date of preparation, or less as determined by repetitive analysis for concentration degradation. Discard the standards when the degradation exceeds 10 percent. (Caution: Contamination may be a problem when a bag is reused if the new gas mixture standard is a lower concentration than the previously contained gas mixture standard.)

7.3.2 Bag Leak Checks. After each use, determine that a bag did not develop leaks. To leak check, connect a water manometer and

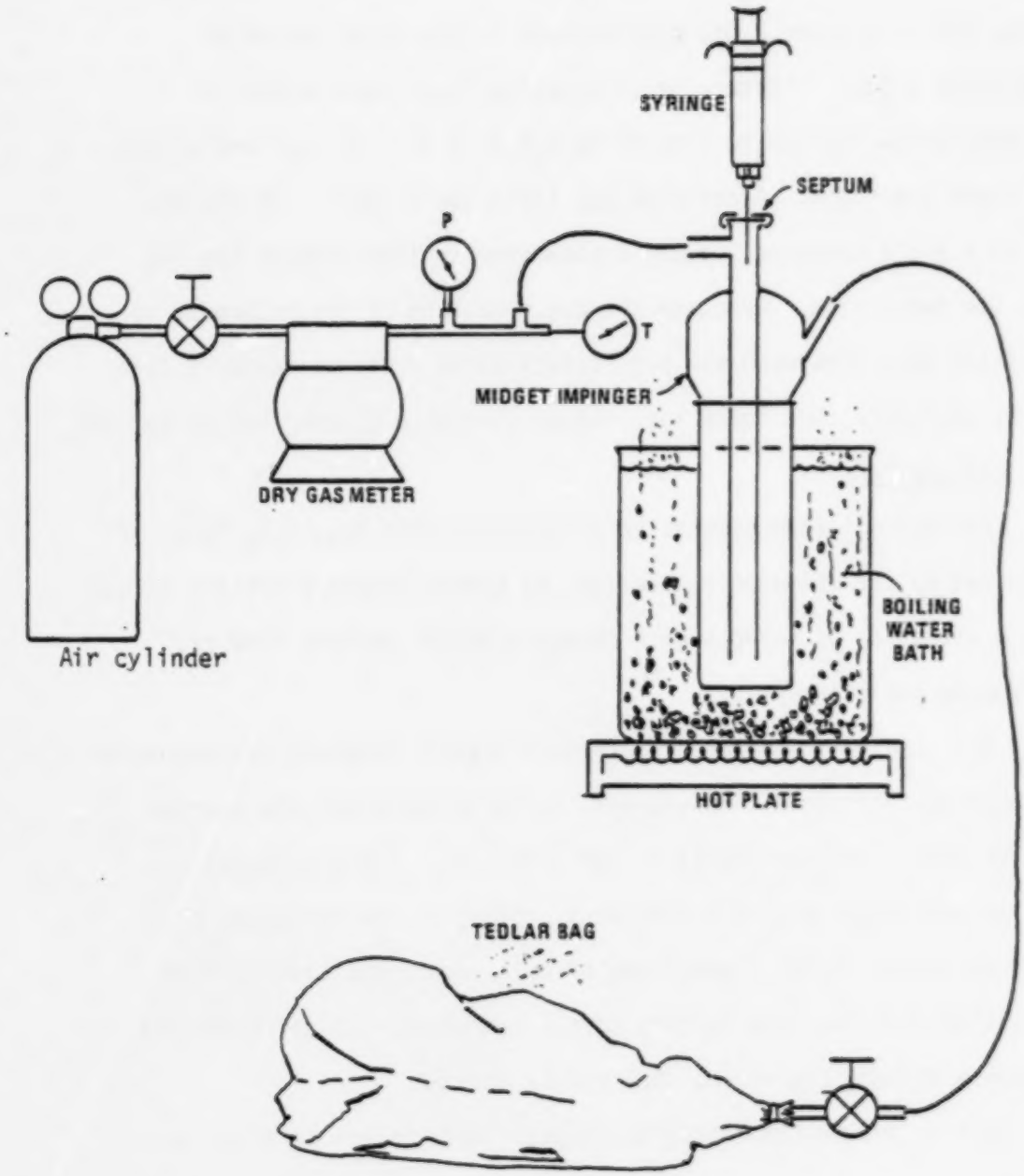

Figure 2. Preparation of standards (optional).

pressurize the bag to 5 to 10 cm H_2O (2 to 4 in. H_2O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. (Note: an alternative leak check method is to pressurize the bag to 5 to 10 cm H_2O or 2 to 4 in. H_2O and allow to stand overnight. A deflated bag indicates a leak.) If the bag is in a rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak. It is advisable that these leak checks also be performed before bag use.

8. Calculations

Correct all measurements or calculations for CH_4, C_2H_6, etc., if required by the emission regulation, by either assuming ambient values are present, or by using source category values derived from gas chromatographic analysis.

8.1 Indicated Carbon or Surrogate Organic Compound Concentration. The surrogate organic compound will normally represent the average carbon number (volume basis) of the emissions. These calculations may assume either a single component organic in the emission, or a constant ratio in the composition of multi-component systems with equivalent FIA response factors to all compounds. If different FIA response factors are known, they can be applied.

8.1.1 Volume Concentration [ppmv]. Results are on a wet gas basis.

8.1.1.1 Concentration as carbon equivalents.

$$C_c = N_c C_r \qquad \text{(Eq. 1)}$$

Where:

C_c = Emission concentration expressed as carbon equivalents.

N_c = Number of carbon atoms per molecule of calibration gas.

C_r = Emission concentration determined by the calibration line.

8.1.1.2 Concentration on the basis of the calibration gas. These values are the C_r values taken from the calibration line.

8.1.1.3 Concentration on the basis of surrogate organic compound.

$$C_s = R_c\, C_r \qquad \text{(Eq. 2)}$$

Where:

C_s = Emission concentration expressed as the surrogate organic compound.

R_c = Ratio of the number of carbon atoms per molecule of the surrogate organic compound to the number of carbon atoms per molecule of the calibration gas.

8.1.2 Mass Concentration [mg/m^3]. The volume occupied by 1 mg·mole of ideal gas at 760 mm Hg and 20°C is 24.040 cm^3. One cubic meter at these conditions would at saturation contain 4.16×10^4 mg·moles, so 1 cm^3 of this volume (1 ppmv) would contain 4.16×10^{-2} mg·moles. Therefore the formula for converting volume concentration to mass concentration is as follows:

$$C_m = 4.16 \times 10^{-2} \text{ mg·moles } C_x M_x \qquad \text{(Eq. 3)}$$

Where:

C_m = Indicated carbon or surrogate organic compound mass concentration, mg/m^3.

C_x = C_c, C_r, or C_s, depending on how the results are to be expressed.

M_x = Molecular weight of carbon, the calibration gas, or surrogate organic compound, mg/mg·mole.

8.2 Source-Specific Organic Standards Concentrations (Optional--see Section 1.1) Use these calculations when the FIA is calibrated with source-specific organic standards. Calculate each organic standard concentration prepared in accordance with Section 7.3 as follows:

$$C = 2594 \frac{B\ d\ T_m}{V_m\ Y\ P_m} \qquad \text{(Eq. 4)}$$

Where:

$$2594 = \frac{760\ \text{mm Hg}\ 10^3}{293°\text{K}} \quad \frac{1000\ \mu\text{g}}{\text{mg}}$$

C = Organic standard concentration, µg/l.

B = Volume of liquid organic injected, µl.

d = Density of the organic at 293°K, mg/µl.

T_m = Absolute temperature of the dry gas meter, °K.

V_m = Gas volume measured by dry gas meter, liters.

Y = Dry gas meter calibration factor.

P_m = Absolute pressure of the dry gas meter, mm Hg.

8.3 Source-Specific Organic Emission Concentrations.

8.3.1 Mass Concentration [mg/m^3]. The emission values in µg/l are taken from the source-specific organic standards response curve.

These values are equivalent to mg/m^3 concentrations and are referred to as C_m values.

$$C_{ss} = \frac{C_m}{4.16 \times 10^{-2} \text{ mg} \cdot \text{moles} \cdot M_{ss}} \qquad \text{(Eq. 5)}$$

Where:

C_{ss} = The emission concentration [ppmv] of the source-specific organic(s).

M_{ss} = Molecular weight of the source-specific organic(s). If the organic emissions consist of two or more compounds, a mass weighted average molecular weight value should be calculated.

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DETERMINATION OF SELECTED VOLATILE ORGANIC EMISSIONS BY THE ADSORPTION COLLECTION TECHNIQUE

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of selected organic compounds that are included in the National Institute for Occupational Safety and Health (NIOSH) Analytical Methods series (see Citation 10.1 under Bibliography).

1.2 Principle. A gas sample is extracted from the stack and the volatile organic vapors are collected on suitable adsorption media. The sample is then analyzed by methods contained in the NIOSH Analytical Methods series. Results are in ppm by volume, on a dry gas basis.

2. Range and Sensitivity

The lower limit of detection varies according to the organic compound being sampled and the total amount of stack gas sampled. For specific details, refer to the appropriate NIOSH method.

3. Interferences

The chromatographic columns and the corresponding operating parameters described in NIOSH methods normally provide adequate resolution. If resolution interferences are encountered on some sources, the chromatograph operator must select the column and operating parameters best suited to his particular analytical requirements. To reduce the chance of a positive bias, it is suggested that the chromatograph operator use two different columns to confirm his analysis.

4. Precision or Reproducibility

The precision or reproducibility of analysis is to be determined for each source and organic(s) application as directed in Section 7.2, and is to be within ±5 percent.

5. Apparatus

Refer to the NIOSH method for the particular organic(s) to be sampled. In addition, the following items are required.

5.1 Sampling

5.1.1 Probe. (Optional) Borosilicate glass or stainless steel, approximately 6-mm ID, with a heating system if water condensation is a problem, and a filter (either in-stack or out-stack heated to stack temperature) to remove particulate matter. In most instances, a plug of glass wool is a satisfactory filter.

5.1.2 Flexible Tubing. To connect probe to adsorption tubes. Use a material that exhibits minimal sample adsorption.

5.1.3 Leakless Sample Pump. Flow controlled, constant rate pump, with set of limiting (sonic) orifices to provide pumping rates from approximately 10 to 100 cc/min.

5.1.4 Bubble-Tube Flowmeter. Volume accuracy within ±1 percent, to calibrate pump.

5.1.5 Stopwatch. To time sampling and pump rate calibration.

5.1.6 Adsorption Tubes. Similar to ones specified by NIOSH, except the amounts of adsorbent per primary/backup sections are 800/200 mg for charcoal tubes and 1040/260 mg for silica gel tubes. As an alternative, the tubes may contain a porous polymer adsorbent such as Tenax GC or XAD-2.

5.1.7 Barometer. Accurate to 5 mm Hg, to measure atmospheric pressure during sampling and pump calibration.

5.1.8 Rotameter. 0 to 100 cc/min, to detect changes in flow rate during sampling.

5.2 Analysis

5.2.1 Chromatographic Columns. Columns as specified in the NIOSH method for the particular organic to be sampled. The analyst may use other columns provided that the precision and accuracy of the analysis of standards are not impaired, and that the information is available for review, confirming that there is adequate resolution of the organic peak(s). (Adequate resolution is defined as an area overlap of not more than 10 percent of each organic peak by another peak. Calculation of area overlap is explained in proposed Appendix C, Supplement A: "Determination of Adequate Chromatographic Peak Resolution," - 45 FR 26682, April 18, 1980).

6. Reagents

Refer to the NIOSH method for the particular organic to be sampled. In addition, the following items are required:

6.1 Audit Standards. Two appropriate solution standards with concentrations unknown to the analyst. The liquid audit samples must consist of a solution containing the organic compound of interest in the same solvent that is used to elute the solid adsorbent. The audit standards must be prepared in the same manner as standards in the respective NIOSH method. The two liquid audit concentrations must be an equivalent gas volume concentration in the range of 5 to 20 ppm and 100 to 300 ppm. When they are available, the tester may obtain audits by contacting: U.S. Environmental Protection Agency,

Environmental Monitoring Systems Laboratory, Quality Assurance Division (MD-77), Research Triangle Park, North Carolina 27711.

7. Procedure

7.1 Sampling. Assemble the sample train as shown in Figure 1. Follow the sampling portion of the NIOSH method section entitled "Procedure." Calibrate the pump and limiting orifice flow rate through adsorption tubes with the bubble tube flowmeter before sampling. The sample system can be operated as a "recirculating loop" for this operation. Record the ambient temperature and barometric pressure. Then, during sampling, use the rotameter to verify that the pump and orifice sampling rate remains constant.

Use a sample probe, if required. Minimize the length of flexible tubing between the probe and adsorption tubes. Several adsorption tubes can be connected in series, if the extra adsorptive capacity is needed. The gas sample must be provided to the sample system at a pressure sufficient for the limiting orifice to function as a sonic orifice. Record the total time and sample flow rate (or the number of pump strokes), the barometric pressure, and ambient temperature. Obtain a total sample volume commensurate with the expected concentration(s) of the volatile organic(s) present, and recommended sample loading factors (weight sample per weight adsorption media). Laboratory tests prior to actual sampling may be necessary to predetermine this volume. When more than one organic is present in the emissions, then relative adsorptive capacity information must be developed. If water vapor is present in the sample at concentrations above 2 to 3 percent, the adsorptive capacity may be severely reduced.

7.2 Sample Analysis. Follow the analysis portion of the NIOSH method section entitled "Procedure." Operate the gas chromatograph according to the manufacturer's instructions. After establishing optimum conditions, verify and document these conditions during all operations. Analyze the audit samples (see Section 8.3), then the emission samples. Repeat the analysis of each sample until the relative deviation of two consecutive injections does not exceed ±5 percent.

7.3 Standards and Calibration. Prepare the standards according to the respective NIOSH method. Use a minimum of three different standards; select the concentrations to bracket the expected average sample concentration. Perform the calibration before and after each day's sample analyses. Prepare the calibration curve using the least squares method.

8. Quality Assurance

8.1 Determination of Desorption Efficiency. During the testing program, determine the desorption efficiency in the expected sample concentration range for each batch of adsorption media to be used according to the respective NIOSH method. Follow the NIOSH procedure with an internal standard. A minimum desorption efficiency of 50 percent must be obtained. Repeat the desorption determination until the relative deviation of two consecutive determinations does not exceed ±5 percent. Use the average desorption efficiency of these two consecutive determinations for the correction specified in Section 9. If the desorption efficiency of the compound(s) of interest is questionable under actual sampling conditions, use the Method of Standard Additions to determine this value.

8.2 Determination of Sample Collection Efficiency. For the source samples, analyze the primary and backup portions of the adsorption tubes separately. If the backup portion exceeds 10 percent of the total amount (primary and backup), repeat the sampling with a larger sampling portion.

8.3 Analysis Audit. Immediately before the sample analyses, analyze the two audits in accordance with Section 7.2. The analysis audit must agree with the audit concentration within ±10 percent.

8.4 Pump Leak Checks and Volume Flow Rate Checks. Perform both of these checks immediately after sampling with all sampling train components in place. Perform all leak checks according to the manufacturer's instructions, and record the results. Use the bubble-tube flowmeter to measure the pump volume flow rate with the orifice used in the test sampling and record the result. If it has changed by more than ±5 but less than ±20 percent, calculate an average flow rate for the test. If the flow rate has changed by more than ±20 percent, recalibrate the pump and repeat the sampling.

9. Calculations

Perform all calculations according to the respective NIOSH method. Correct all sample volumes to standard conditions. If a sample dilution system has been used, multiply the results by the appropriate dilution ratio. Correct all results by dividing by the desorption efficiency (decimal value). Report results as ppm by volume, dry basis.

10. Bibliography

10.1 NIOSH Manual of Analytical Methods, Volumes 1, 2, 3, 4, 5, 6. 7., U.S. Department of Health and Human Services, National Institute for

Occupational Safety and Health, Center for Disease Control, 4676 Columbia Parkway, Cincinnati, Ohio 45226. April 1977 - August 1981. May be available from the Superintendent of Documents, Government Printing Office, Washington, D.C. 20402. Stock Number/Price: Volume 1 - 017-033-00267-3/$13, Volume 2 - 017-033-00260-6/$11, Volume 3 - 017-033-00261-4/$14, Volume 4 - 017-033-00317-3/$7.25, Volume 5 - 017-033-00349-1/$10, Volume 6 - 017-033-00369-6/$9, and Volume 7 - 017-033-00396-5/$7. Prices subject to change. Foreign orders add 25 percent.

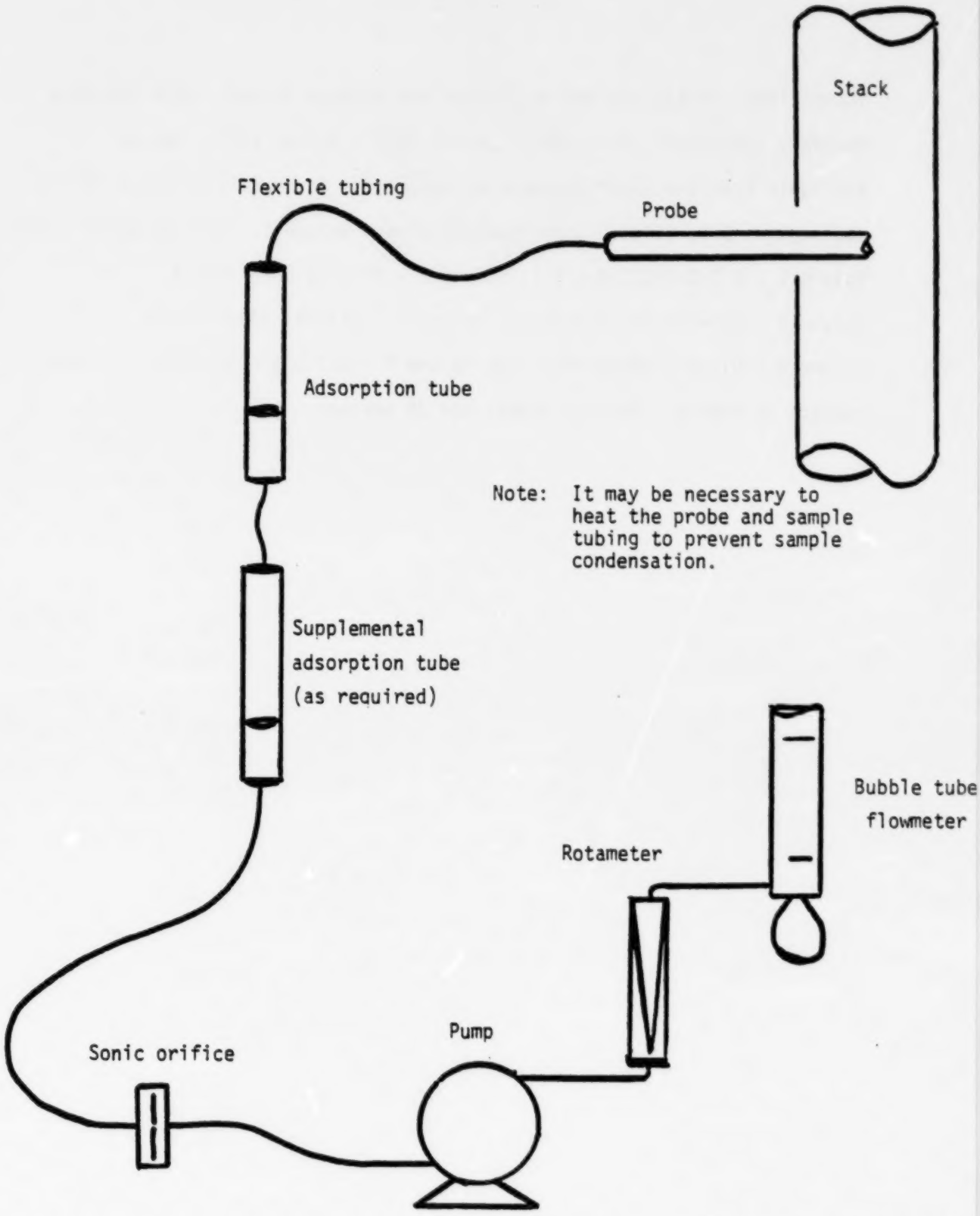

Figure . Adsorption tube sampling method.

APPROXIMATE DETERMINATION OF SELECTED VOLATILE ORGANIC EMISSIONS USING DETECTOR TUBES

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of individually selected volatile organics in source gases only when the extent of detector tube reactions with all other gases present in the source gas is known. An overall positive bias in the measurements is acceptable if the emission values thus generated are still acceptable for the purpose of the sampling. However, biased results must be protected from improper use.

1.2 Principle. A previously collected or instantaneous sample of source gas is drawn through a glass tube that contains a chemical reagent on an adsorbent by a calibrated sampling pump. This chemical reagent is selected for its colorimetric reaction with the gas in question. The length of the color change or stain is measured, and is indicative of the volume concentration. If a desiccating pre-layer is present in the detector tube, results are on a dry basis.

2. Concentration Range and Sensitivity

The concentration range and sensitivity of this method can be varied by the amount of sample gas drawn through the tube, or by the chemical reactions employed. Refer to literature from the detector tube manufacturer for the particular analysis desired.

3. Interferences

Refer to the manufacturer's instructions furnished with the tubes employed. The information provided by the detector tube manufacturer about interfering gases may not be sufficient to determine the applicability of a given detector tube to a given source gas. Therefore, detector tubes shall only be used on sources where the relationship between concentrations reported by detector tube analysis and some other approved analytical technique has been established through comparative sampling.

4. Apparatus

4.1 Sample Pump. Piston type detector tube pump, 100 cc/stroke, such as Mine Safety Appliance, Bendix Gastec, Matheson-Kitagawa, Draeger, or equivalent. Use a pump from the same manufacturer as the detector tubes used.

4.2 Detector Tubes. Selected for the gas(es) to be measured and the expected concentration range, with instruction sheets, lot identification, and expiration dates. Store tubes according to the manufacturer's instructions.

4.3 Sampling Probe. Glass or stainless steel, heated as required, of sufficient length that the exit gas temperature will be regulated to the approximate temperature at which the detector tube was calibrated by the manufacturer. If studies indicate this temperature is particularly important, a thermometer in a tee fitting attached to the exit end of the sampling probe is also required.

4.4 Filter. Required if particulate matter is present that could clog detector tube inlet.

4.5 Flexible 1 Liter Sample Bag and Inert Leakless Pump. Required if the pressure of the source differs by more than 3 percent from atmospheric pressure.

4.6 Condenser. Required if water vapor or other condensible material is present in the gas to be sampled in quantities sufficient to plug the filter or detector tube.

4.7 Barometer. Accurate to 5 mm Hg, to measure atmospheric pressure during all analyses.

4.8 Thermometer. Accurate to 1° C, to measure atmospheric temperature during all analyses.

4.9 Audit Cylinder Standard. Appropriate gas mixture standard with concentration known only to the person supervising the analysis of samples. It is preferable that the audit cylinder standard be prepared according to the procedure in proposed Method 23 (45 FR 39776, June 11, 1980). Some detector tubes respond correctly only in the presence of moisture and oxygen, in which case these gases must be included in the audit standard. The concentration of the audit cylinder should be within a factor of one-half to two of the expected stack gas concentration. When it is available, the tester may obtain an audit cylinder by contacting: U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division (MD-77), Research Triangle Park, North Carolina 27711.

5. Procedure

5.1 Sampling and Analysis. Assemble and use the apparatus according to the manufacturer's instructions. If the source pressure is within 3 percent of atmospheric and no condenser is required, use the piston pump to purge the probe and then draw sample into the detector tube.

If the source pressure is greater than atmospheric, use a gas tight probe fitting at the stack and allow the probe to purge. Then attach and fill the flexible sample bag with source gas. If the source pressure is less than atmospheric, use an inert leakless pump to purge source gas through the probe, and then fill the flexible bag. For those instances where a flexible sample bag is required, withdraw the analysis sample from the sample bag with the piston pump as soon as possible after the bag is filled.

Record the expiration date of the tubes, atmospheric temperature and barometric pressure, and volume sampled.

Note the length of stain or color change produced on each tube, and the length of time the stain was allowed to develop. Record the indicated concentration of each tube. Repeat the analysis until either of two consecutive tubes do not deviate more than $\pm$25 percent from their average. Each average value constitutes one result.

If condensation of water or other material interferes with operation of the detector tube, a small condenser may be used between the sample probe and the flexible bag, however, sample loss may occur. Lowering of the source gas dew point by pumping the source gas into an inert sampling bag containing a known volume of zero air via an inert, leakless pump may also be employed. If the manufacturer's instructions for the tubes employed prescribe a humidity correction, then devise and use some means of measuring the sample gas relative humidity.

6. Quality Assurance

6.1 Analysis Audit. Immediately before the sample analyses, perform analyses on the audit cylinder by following the procedure in Section 5.1. The analysis audit results should agree with the cylinder concentration within ±25 percent.

6.2 Flexible Bag Leak Checks, Pump Leak Checks and Pump Volume Checks. Perform all of these checks immediately after sampling and analysis. Perform bag leak checks according to Method 23. Perform all pump checks according to the pump manufacturer's instructions. Record all results.

7. Calculations

Correct each sample concentration result as indicated on the detector tube according to the detector tube manufacturer's instructions for temperature, humidity and pressure. Normally, pressure is the only significant correction required.

8. Bibliography

8.1 Bendix, Inc. Gastec Precision Gas Detector System Manual. Bendix Environmental and Process Instruments Division, Drawer 831, Lewisburg, West Virginia 24901.

8.2 Mine Safety Appliance Company. Instructions for Operation and Maintenance of M.S.A. Universal Sampling Pump. Pittsburgh, Pennsylvania 15208.

8.3 Method 23. Determination of Halogenated Organics from Stationary Sources. 45 FR 39776. Proposed June 11, 1980.